

SCIENCE REQUIREMENTS DOCUMENT

Binary Critical Aggregation Test – 4 (BCAT-4)

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1. Executive Summary

1.1. Description of Experiment

The goals of this International Space Station (ISS) bench top experiment are twofold: (1) to further investigate critical, fundamental problems in colloid science, (2) and to evolve the field of ‘colloid engineering’, which creates materials with novel properties using colloidal particles as precursors. In both cases, gravity-driven sedimentation and convection precludes these experiments from being carried out on earth, and requires a microgravity environment to address the most critical questions.

This experiment is envisioned as a direct follow-on to the Binary Colloid Alloy Test 3 (BCAT-3), which itself is a follow-on to several microgravity flight experiments, including the Physics of Colloids in Space (PCS), earlier iterations of the Binary Colloid Alloy Test (BCAT, BCAT-2), and Colloidal Gelation (CGel). This benchtop experiment will also provide science results and optimize sample selection for PCS-2 and the Low Volume-Fraction Entropically-Driven Colloidal Assembly (LΦCA) experiments, which are currently scheduled to fly in the Light Microscopy Module (LMM) aboard the ISS starting in 2006.

This experiment will focus on two classes of colloidal samples: critical point colloid-polymer mixtures, and crystallization of spherical colloids at high volume fractions. Understanding critical phenomena was an important theoretical advance in physics during the last half century, but ground-based experiments have been limited by gravity. A gravitational field invariably causes a denser liquid phase to fall to the bottom of any container, preventing direct observation of the spatial structure of phase separation over the long term. In the absence of gravity, however, we can watch the boundary between separating phases and it does not look at all the same as on earth. The microgravity environment allows the phase boundary to assume its true thermodynamically-driven shape.

Our first set of samples is mixtures of colloids and polymers near their liquid-gas critical point. The second set consists of spherical colloidal particles with effective volume fractions resulting in an amorphous or glassy phase in normal gravity. Earlier experiments (Colloidal Disorder-Order Transition, CDOT-1 & CDOT-2) have observed that gravity plays an overwhelmingly important role on the crystallization and glass-formation behavior of spherical colloids. We expect similarly significant effects, and explore this in the new system of colloids in which we adjust the size polydispersity. For all sets of samples, we will mix the samples, and then let them evolve into phase-separating liquid-gas mixtures, or crystals, whose time evolution we will monitor with a camera. Although simple in setup and execution, BCAT-4 has the unique ability to provide important data on experimental systems that cannot be accessed on earth, and will therefore, like its predecessor flight experiments, be able to contribute to our fundamental understanding of the thermodynamics and kinetics of colloids in particular, and materials in general.

1.2. Scientific Knowledge to be Gained

Data from the BCAT-3 critical point samples indicate that the present theory for the critical behavior of atomic or molecular fluids (for which Kenneth G. Wilson was awarded the 1982 Nobel Prize) may not completely describe the evolution of colloid-polymer mixtures. When the masking effects of gravity are removed, the rate at which the BCAT-3 critical point samples separate into two phases show an unexpected exponential scaling law behavior. This result is in direct contrast to the normally observed phase separation which can be modeled by a power law. These BCAT-4 experiments are essential to the understanding of the origin of this unusual scaling, and to providing quantitative data for theorists to model. Because BCAT-4 will follow the evolution of samples for days or months (as the samples will evolve, even in storage) in the microgravity environment, there is simply no other way to gain this important class of data.

BCAT-3 is the first experiment to use the size advantages of colloids, which can be used as model atoms, to systematically and precisely locate the critical point and characterize the behavior around it. These larger particles are not only large enough to scatter light (and thus be visible to the camera, as well as the naked eye), but also large enough to slow down the dynamics to speeds that allow us to photograph the phase separation of samples over a period of weeks, assisted by apparatus already onboard the ISS.

Moreover, increased knowledge of some of the areas of this basic physical research may have future benefits in the application of the same physical processes on earth. Supercritical fluids (fluids possessing properties of a gas and a liquid simultaneously) have numerous applications in a wide variety of fields. An example is supercritical carbon dioxide, which represents a solvent that can perform a wide variety of extraction and processing duties, an environmentally friendly solution replacing toxic solvents used in dry cleaning, decaffeination of coffee beans, and extraction of delicate pharmacological molecules from plants for use in new drugs. The development and use of newer supercritical fluids is dependent on further understanding of the critical point of those fluids, which the BCAT experiments are providing. In addition, the specific dynamics of these colloid-polymer mixtures are of great economic importance to product stability: if phase separation occurs during the shelf-life of certain household products, then their value to the consumer evaporates. There is thus a significant commercial incentive, in a market worth billions of dollars annually, in coming to a better fundamental understanding of this particular system, and BCAT-4 will certainly aid that process.

The so-called ‘model hard-sphere’ particle suspension experiments (samples 8–10) will extend our understanding of known self-assembly and thermodynamics processes in complex fluids. Clean observations of phase transitions in the microgravity environment will provide much needed insight about the interplay of polydispersity and sedimentation in affecting phase behavior. These effects are normally masked in experiments on earth. Traditional questions about the relative packing fractions, which crystallization phase is manifested, and the passing from one phase to the other, can be studied in these systems with exquisite resolution without the perturbing effects of sedimentation.

1.3. Value of Knowledge to Scientific Field

Because the BCAT-3 and BCAT-3+ experiments have forced us to question the applicability of existing molecular theory for critical phenomena to colloid-polymer mixtures, seven of these ten samples (samples 1–7) will be critical point samples. All of the BCAT-3 samples fell along a straight line in the phase diagram, and BCAT-4 will allow us to probe surrounding points, allowing a far more precise location of the critical point (which has never been carefully located in these systems), and will provide the quantitative data needed by theorists to confirm new models of what is happening.

Samples 8–10 are of a different class. They will consist of spherical colloidal particles whose size uniformity is tuned to either suppress crystallization or increase the rate at which crystals nucleate using spherical seed particles. The results of this experiment have important consequences for the control of the resulting crystal size distribution. BCAT-4 represents a significant opportunity to explore the fundamental physics behind these processes by crystallizing in microgravity where there is no gravitational jamming to kill the natural ordering process.

1.4. Justification of the Need for a Space Environment

Both critical point and hard-sphere crystal samples are dramatically affected by the effects of gravity. In BCAT-3, we observed the formation of a bicontinuous network in microgravity that coarsened over time until complete phase separation was achieved. On the ground, by the time significant phase separation has begun, all of the particles have settled to the bottom of the sample chamber. Consequently, bicontinuous networks never form on earth.

Similarly, the formation of colloidal crystals is strongly affected by sedimentation; this has most graphically been demonstrated by the results of the experiments of Chaikin and Russel, who showed that the morphology of colloidal crystals grown in space is completely different from that grown on earth. The primary reason for this is sedimentation: as the crystals sediment, the shear of the fluid flowing past their edges is sufficient to destroy them. In addition, the sedimentation time of the crystals rapidly begins to compete with the diffusion time of the accreting particles, significantly changing the growth mechanism.

If a crystal forms, we will place a ‘mini-MagLite’ flashlight (like the one we used in BCAT-3) behind the sample to illuminate it and see if the camera can photograph any colors that result when white light passes through a crystal and gets diffracted. If this does happen, we will then fix the camera at that position, rehomogenize the sample and use EarthKAM to watch the sample crystallize over a period of days to weeks.

Clearly, these effects can be mitigated to a certain degree on the ground, by changing solvents to a nearly buoyancy-matched combination. However, these heavy organic solvents invariably swell the colloidal particles, which then selectively absorb the heavier solvent and gain density. It is therefore impossible on the ground to conduct an experiment where the particles remain buoyant for the months or longer it takes to

observe the processes we have already seen in BCAT-3 and earlier crystallization experiments. By the time these processes have occurred, the particles in density-matched solvents have changed their density slightly and settled to the bottom of the sample chamber. The microgravity environment is therefore absolutely crucial to our ability to conduct these experiments and investigate these fundamental physical processes.

2. Background

2.1. General Description of the Scientific Field

The conceptual motivations for this work are coupled to current research in complex fluids, optics, and many-body statistical physics. The bulk of our research centers on the physics of complex fluids, an emerging subfield of condensed matter physics. Complex fluids are soft materials such as colloidal suspensions, emulsions, polymer solutions, membranes, and mixtures thereof, whose structure and dynamics are strongly influenced by entropy and by relatively weak mechanical forces. They are thus particularly well suited for the microgravity environment of the ISS where the main mechanical force, gravity, is severely reduced. In this proposal we focus on mixtures of colloidal particles and other soft materials. These materials are intriguing from both fundamental and practical points of view.

Research on these substances is also driven by a variety of practical applications (see for example [72] and references therein) ranging from the prospect of using these materials as templates for photonic materials [73–75] and lithography [76,77], to their uses in ceramics and as biochemical sensors [78,79]. In a different vein, studies of complex fluids are increasingly stimulated by analogies from cell biology [80,81], and in some cases provide critical insights about mechanisms that arise in the crowded, aqueous, and near-room-temperature cellular environments. In still other systems, particle additives offer practical control of fluid rheologies, thus improving the performances of conventional materials such as paints, motor oils, food and cosmetics.

In BCAT-4, we focus on colloidal suspensions, which exhibit a rich and varied range of properties. They are of great scientific interest, as well as of great practical importance. They can be synthesized with exquisite precision and control, and can be formed from a wide range of materials. Colloidal particle distributions can be made highly monodisperse. The interactions between the particles can also be finely tuned, and can vary from repulsive to attractive, over a controllable range. The particles can be induced to self-assemble into a wide range of structures, many of which have long-range order. They can serve as model systems for the study of fluid and solid properties, with the colloidal particles playing the role of thermodynamically-driven atoms or molecules. The relaxation times that characterize their behavior are much longer than those of atomic or molecular materials, making them much more accessible to experimental probes on the benchtop scale. In addition, the larger size of the colloidal particles facilitates the study of the structure and dynamics of the suspensions, allowing, for

example, the use of optical techniques such as static and dynamic light scattering and laser crystallography, or Bragg scattering.

Colloidal suspensions exhibit a wide range of structures, both ordered and disordered, with correlations that often extend to the size of the system. Furthermore they exhibit a wide range of dynamics, which can often be tied closely to the structure of the system. Their rich phenomenology derives from a fascinating interplay of physical, chemical and hydrodynamic mechanisms whose realization provides a unique opportunity for the study of statistical mechanics in classical many-body systems. Recent experimental and theoretical progress relevant to the present proposal includes studies of the role of entropy and interparticle interaction in affecting self-assembly [1] and directed assembly in systems of monodisperse hard-spheres [2–12], particle suspensions with added particles or polymers [13–52], monodisperse emulsions with added polymer [41,43], binary emulsions [38], suspensions of rod-like particles in mixtures of spheres [53–60], liquid crystal emulsions [61–63], and charged-stabilized particle suspensions [64–71].

The high degree of control over the synthesis of colloidal particles and our ability to finely tune the interaction between them also makes it possible to use colloidal particles as precursors for forming new materials; these should have unique and novel properties. This new route to materials synthesis has come to be called ‘colloidal engineering’, allow the formation of materials with unique and fascinating properties. For example, these alloys may form the precursors for very high quality ceramics. Alternatively, one set of particles could be plastic and the other set of particles could be a metal or a semiconductor. After formation of the binary superlattice, sintering at a temperature above the glass transition of the plastic could provide a plastic sheet containing the other particles in ordered arrays. Such a material should have unique optical, or even electronic, properties. For example, this may be a simple method for fabricating an array of quantum dots that has useful optoelectronic properties. Alternatively, colloidal engineering may provide a simple route to the synthesis of photonic band gap materials [6,7], or structures that have a greatly reduced phase space available for radiation [8].

Current routes for fabricating photonic band gap materials in the optical regime rely on three-dimensional lithography, which is a very challenging and difficult process. Colloidal engineering may offer a simple method for making these materials that completely bypasses many of these difficulties. These superlattices could also be used as novel optical switches or displays. For example, instead of using solid colloidal particles, monodisperse emulsion droplets or colloids filled with liquid crystal molecules could be used to form the structures, allowing their optical properties to be switched by application of an external electric field. The switching voltage is a function of the particles size, making it feasible to switch a Bragg scattering matrix on and off by manipulating only the large droplets in a superlattice, thus making the smaller one Bragg scatter. This technique could form the basis for a novel optoelectronic display technology that not only switches light, but also controls the direction or color of the displayed light. Many other novel materials can be envisioned.

2.2. Proposed Experiments

The results from BCAT-4 will greatly enhance our knowledge of critical phenomena for an important class of complex fluids. Moreover, three of these samples will indicate how size uniformity at high number density affects crystallization in microgravity. Additionally, the science results that are returned by this work will impact future experiments with colloids, and possibly those being done in microgravity, where the masking effects of sedimentation, convection, and particle jamming are removed.

2.2.1. *Colloid-Polymer Mixtures*

One of the most interesting features of the colloid-polymer phase diagrams are the regions of coexistence between several different phases, particularly near a critical point in their phase diagram. An important result from BCAT-3 was establishing that samples that phase separate on earth will also do so in microgravity. However, the temporal dynamics, and evolution of spatial structure, cannot be observed on the ground because the earth's gravity inevitably drives the heavier colloidal liquid phase, with a higher colloid concentration, into the bottom of the sample chamber, typically within hours or days. The delicate structures formed during phase separation in microgravity, however, take weeks to months to form, which cannot be observed on earth even with the best attempts to match buoyancy. However, as the photographs from the CGel experiment highlighted, the structures that do form can provide considerable information about the kinetics of the phase separation and the coexisting states.

Some of the most important questions arise from the study of the fluid phase. For example, it is not clear whether fluid drops are formed in all cases upon phase separation. If they are, it would be very interesting to determine their surface tension, as it must play a critical role in their formation. This could be done through a study of the shape of the droplets and a determination of the surface fluctuations. In addition, it would be very interesting to determine the dynamics of the liquid within the droplets, which could be done by dynamic light scattering, provided a single droplet could be isolated in the collection volume. It would also be interesting to determine the nature of the crystallization when a solid is present. The crystals may first form in the liquid droplets, and if this is the case, they should markedly modify the nature of the fluid within the drops. Alternatively, they may also sublime from the gas phase. Resolution of these questions may lead to finer control over the crystal structures that form, improving their potential uses for engineering new materials. Finally, the properties of the fractal colloidal aggregates will be studied by directly imaging their structures. In addition, by following the thermal motion of these structures with time, we will also study the dynamics of these structures, and will probe the excitation spectrum of the fractal aggregates.

To study these effects, it is essential to be able to isolate the individual components. This can be accomplished by imaging the sample to identify the structures; they can also then be studied to determine effects such as where crystals form, and how the shape of the fluid droplets fluctuate. However, once the structures are isolated, it will also be important to use scattering or imaging techniques to increase our knowledge of

their properties. For example, correlation studies with series of images from confocal microscopy can provide critical information about the interparticle interactions within the fluid droplets. It can also provide some insight into the properties of the crystallites. Similarly, the structure of the crystallites is most easily determined through confocal microscopy. In all these cases, if we were to use light scattering methods, it is essential that only a single component be present in the scattering volume; otherwise the interpretation of the scattered intensity is greatly complicated. Confocal microscopy is the ideal method to achieve this, which allows very small volumes to be imaged and can also be adapted to allow scattered light to be collected from this same volume.

2.2.2. *Glass phase vs. crystallization at high volume fractions*

In previous NASA microgravity experiments, we discovered that colloidal suspensions in the volume fraction range 0.58–0.64 which showed glassy behavior but did not crystallize in 1-g, readily formed crystals in microgravity. Although experiments by others on density matched samples in normal gravity later tended to confirm these results, their samples were far from ideal hard particles due to interactions inherent in the density matching process. We therefore plan to extend these microgravity experiments in BCAT-4 by seeing the effects of polydispersity on crystallization in this volume fraction range. The contrasting samples will be as monodisperse as possible (*e.g.*, < 5%), a slightly polydisperse sample and a bi-disperse sample, mostly one average particle size, but with a few large particles (~ 7 times the average particle radius) to provide crystal nucleation sites.

2.3. **Current Research in Support of Proposed Experiments**

Much of the current research effort is associated with the preparations for the flight experiments. In addition, more data analysis is being carried out for the flights that have already taken place, primarily to attempt to learn as much as possible from the photographs, through the use of improved digital image processing.

Concurrently, the near buoyancy match significantly extends the amount of ground-based preparatory research that can be done. Current work at Harvard University is exploring the dynamics of gels, which appear to be driven by the same phase separation processes that occur near the critical point. However, by moving far away from that point in the phase diagram, we reach a regime where the rate of phase separation is far faster, so that the near buoyancy-matched samples can be imaged in the time frame where the particles still remain buoyant (days on the ground, not months as in microgravity). Moreover, we have also observed cluster phases on the ground, and current work is seeking to find out if, in fact, these clusters are created by the same processes that create freely-circulating clusters in the microgravity environment of the ISS.

Research is being carried out to learn how to synthesize new particles. At NYU, Hollingsworth is developing the synthesis routes required to make aspherical particles. New methods are being developed that require the use of much smaller quantities, making it feasible to synthesize the required material.

2.4. Anticipated Advance in the State of the Art

Addressing the questions proposed above would significantly increase our understanding of the properties and behavior of colloidal suspensions. In particular, BCAT-3 has approached phase boundaries near the critical point to a much closer degree than any others, primarily because the microgravity environment allows observations for the far longer time scales that occur near the critical point. The hard-sphere particle crystallization experiments will provide crucial guidance in the use of colloidal precursors for materials synthesis, and would help establish colloidal engineering as a new synthesis route.

3. Justification for Conducting the Experiment in Space

3.1. Limitations of Ground-Based Testing

The primary limitation with ground-based work results from sedimentation. A second less critical problem arises due to convection effects, which are also gravity induced. Both of these effects will be greatly reduced in microgravity. A basic understanding of the limitations imposed by gravity comes from the problems encountered in current experiments. We review these first, and then discuss more detailed estimates of the effects of gravity, even in the optimum case.

Experiments at the University of Edinburgh have probed the formation and structure of crystals from monodisperse colloidal particles using microscopy. Small capillary tubes (~ 2 mm wide \times $100\text{ }\mu\text{m}$ thick) were used as sample cells. The samples were loaded in a fluid state, the cell was sealed and the measurements begun. In the course of about an hour, the samples crystallized. The crystallization process was studied and the final structures were determined by imaging. However, during the course of the experiment, it was inevitably noticed that the particles sediment, so that the top of the cell has a lower density, which typically remains fluid, while the bottom has a higher density, where the crystals form. Thus, it is impossible to accurately set the volume fraction. Moreover, the sample at the bottom is always under the additional osmotic pressure of the sample above and this result has a direct effect on the sample properties. As shown by the results of the CDOT experiment, the morphology of the crystals is significantly modified by the gravity-induced settling. This behavior limits the size of the crystals that grow, which will place a significant limitation on their use for materials growth.

Experiments conducted by Segrè at Penn and at Harvard also highlight the effects of gravity. He used time lapse video to record the formation and growth of the crystals from larger scale samples, again of monodisperse particles. He first used the standard mixture of index-matching fluids, tetralin and decalin, for which there is a density mismatch of $\Delta\rho \approx 0.25\text{ g/cm}^3$. Thus the colloidal crystals observed tended to sediment rapidly. He then repeated the experiment using cycloheptyl bromide, which can be used to achieve a more nearly buoyancy matched sample while still index matching the PMMA particles. He estimated that the density mismatch was decreased by about two orders of magnitude, to $\Delta\rho \approx 0.002\text{ g/cm}^3$. This is probably an optimistic estimate, with

the actual density match being poorer; however, while the sedimentation velocity was reduced, and the crystals were larger and more dendritic, they also clearly continued to sediment. Because of uncertainties in mixing volumes, it is unlikely that density matching closer than this can be achieved; differences in thermal expansions also limit the exact buoyancy match. In addition, the only way to reliably and accurately set the volume fraction of the samples is to take advantage of their phase behavior. Their volume fraction, ϕ , can be adjusted to be in the two-phase region, with $0.50 \leq \phi \leq 0.55$, where both the fluid and crystal coexist. The fluid has a volume fraction equal approximately to this lower bound, while the solid corresponds to the larger volume fraction. By allowing the denser crystals to sediment to the bottom of the sample, the volume fraction of the supernatant fluid is set at $\phi = 0.5$. Accurate adjustment of the volume fraction is essential for all experiments, and this procedure has proven to be the most reliable and accurate method. Thus, even the slow sedimentation of the near-density matched samples is highly desirable.

A final observation about gravity induced effects comes from some of the results obtained in the CGel glovebox experiment. In this experiment, samples remained in microgravity for about four months at which time they were photographed. Although the results are not entirely certain (no light scattering was performed), some of the pictures seem to show a noticeable difference in apparent photographic density from the top to the bottom of the cell. One explanation for this observation is that the material had sedimented slightly during the course of the experiment. Thus, it may actually be desirable to use as close to buoyancy matched particles as are available in the microgravity experiments to minimize this effect for the most delicate of samples and the longest duration experiments.

We can make several estimates of the effects of gravity on the crystals. The first one is to calculate when sedimentation can compete with diffusion for the growth of the crystals. The concept here is that a free crystal grows by diffusion of the accreting particles to the surface. Competing with this is the sedimentation of the whole crystal. We can estimate an effective Peclet number, Pe_{eff} , which expresses the ratio of the time for a single particle to diffuse its own size, t_D , to the time for the crystal to sediment a single particle size, t_C . We might expect that when $Pe_{\text{eff}} = t_D/t_C \sim 1$, the effects of sedimentation will become significant. This will allow us to estimate a maximum crystal size that can be achieved. We do this for crystals from monodisperse particles as all the required parameters are known for them.

The buoyant mass of a crystal of typical radius R_C is given by

$$m_b = 8\Delta\rho_p \Delta\rho R_c^3 \quad (1)$$

where $\Delta\rho_p = 0.05 \text{ g/cm}^3$ is the difference in particle density between the crystal and the fluid, while $\Delta\rho$ is the intrinsic difference in density between the particles and the surrounding fluid. The sedimentation velocity can then be calculated by balancing the gravitational force on the crystal with the Stokes drag of the fluid, resulting in

$$v_c = \frac{\Delta\rho_p \Delta\rho g R_c^2}{6\pi\eta} \quad (2)$$

where g is the gravitational acceleration constant and η is the viscosity of the surrounding fluid, which we take to be the value of the viscosity of the fluid phase which is about 50 times that of the solvent. The characteristic times are then

$$t_c = \frac{R}{v_c} \text{ and } t_D = \frac{R^2}{D},$$

where D is the diffusion coefficient of the single particles. This value can be calculated using the Stokes-Einstein relation,

$$D = \frac{k_B T}{6\pi\eta R} \quad (3)$$

where T is the absolute temperature and k_B is Boltzmann's constant. It follows that the effective Peclet number for this form of crystal growth is,

$$Pe_{\text{eff}} = \frac{8\Delta\rho_p \Delta\rho R_c^2 R^2 g}{k_B T}. \quad (4)$$

If we use $Pe_{\text{eff}} = 1$ as a criterion for when sedimentation becomes important, we can determine the maximum crystal size that can grow under different conditions,

$$R_{C,\text{max}} = \sqrt{\frac{k_B T}{8\Delta\rho_p \Delta\rho g R^2}} \approx \frac{3 \times 10^{-7}}{R \sqrt{\Delta\rho g}} \text{ cm} \quad (5)$$

using CGS units. If we use $R = 0.5 \mu\text{m}$, we can calculate the size of PMMA crystals that can be formed on earth with the standard index matching solvents, decalin and tetralin, for which $\Delta\rho \approx 0.25 \text{ g/cm}^3$ and $g \approx 10^3 \text{ cm/s}^2$. Substituting the appropriate values into Eq. (5), we obtain a value of $R_{C,\text{max}} \sim 4 \mu\text{m}$. This result is consistent with the observation that dendritic crystals are never observed on earth. The value of $R_{C,\text{max}}$ varies inversely as the square root of both g and $\Delta\rho$, allowing us to estimate the effects of both buoyancy matching in microgravity. If we improve the buoyancy match by two orders of magnitude, the size of the crystals will increase by one order of magnitude to $R_{C,\text{max}} \sim 40 \mu\text{m}$. By comparison, using the standard non-buoyancy matched fluids, but doing the experiment in microgravity increases the maximum crystal size three orders to about $R_{C,\text{max}} \sim 4 \text{ mm}$, again consistent with what was observed in the CDOT experiments. Combining the approaches of near buoyancy matching and microgravity could produce crystals of remarkable sizes, $R_{C,\text{max}} \sim 4 \text{ cm}$!

Of course, these are the simplest cases to consider. The key is the square root dependence on both $\Delta\rho$ and g . Thus even a far less favorable density mismatch of 20

would decrease the size of the crystals by a factor of 10, while microgravity would still provide the benefit of a factor of 10^3 . As a result, we might estimate $R_{C,\max} \sim 400 \mu\text{m}$ in the most unfavorable case of binary alloys with a large density mismatch, provided we do the experiment in microgravity. This size is still quite reasonable for making materials with interesting optical properties.

Finally, it is also interesting to estimate the actual sedimentation velocity for some cases. Using Eq. (2), and assuming a $100 \mu\text{m}$ crystal of PMMA in decalin and tetralin in microgravity, $v_C \sim 0.5 \mu\text{m/sec}$ on earth, where we have assumed that $\eta = 1$ Poise. In microgravity, this is reduced by 10^6 , becoming more like about $v_C \sim 1 \mu\text{m/month}$.

In evaluating the significance of these calculations, we feel that the estimates for the monodisperse PMMA crystals are probably more relevant to the glassy PMMA and colloid-polymer mixtures.

3.2. Limitations of Drop Towers

The length of time required for the formation of any of these structures is far too long for short-term microgravity experiments, such as those performed in a drop tower. In this arrangement, low gravity is achieved only for a few seconds. The phase separation of colloid-polymer mixtures can take several minutes to many days. And the crystallization of the hard sphere samples can take days to weeks.

3.3. Limitations of Testing in Aircraft

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in an airplane. For example, in the parabolic flight of the 'C-9 Low-G Flight Research' aircraft, low gravity is only achieved for less than a minute. The phase separation of colloid-polymer mixtures can take several minutes to many days. This behavior is thus too slow for either a drop tower or an airplane experiment. And the crystallization of the hard sphere samples can take days to weeks.

3.4. Need for Accommodations on the Space Station

The space station provides an environment where microgravity is sustained long enough to allow these experiments to be conducted. The samples can be homogenized by mixing them and then can be allowed to develop under microgravity for an extended period of time without astronaut intervention in the mean time. Their structure and properties can then be probed in situ allowing the unique behavior of the new materials to be studied.

3.5. Limitations of Mathematical Modeling

Data from the BCAT-3 critical point samples indicate that the present theory for the critical behavior of atomic and molecular fluids (for which Kenneth G. Wilson was awarded the 1982 Nobel Prize) show that a direct application of the theory may not describe all of the observations we have made on ISS. When the masking effects of gravity are removed, the rate that BCAT-3 critical point samples separate into two phases show an unexpected (exponential scaling law) behavior, which seems to deviate from expected (power law scaling) behavior. These experiments are essential to understand the origin of the behavior. Thus, further experiment will provide additional guidance for further refinement of the theory.

The effects of polydispersity and spherical ‘seed’ particles on the crystal nucleation barrier and the structure of the critical nucleus have been examined by Frenkel, *et al.* [26,27]. The recent numerical simulations make predictions concerning the structure and free energy of colloidal crystal nuclei which will be tested. Classical nucleation theory does not capture the general experimental observation that the rate of crystal nucleation passes through a maximum as the supersaturation is increased. The experimental results obtained in microgravity should be very helpful in directing future modeling and will provide the experimental input that is critical for forming and testing new models.

To date, only equilibrium simulations can accommodate sufficient numbers of particles to convincingly treat ordered systems. With non-equilibrium processes the necessity for long run times due to the slow dynamics and the importance of detailed hydrodynamic interactions have prevented progress, except for 10^1 – 10^2 particles in a simple shearing flow. This precludes for the foreseeable future definitive consideration of interesting problems related to the hard sphere transition, such as the nucleation and growth of the solid phase, shear induced order and shear induced melting, and the linear viscoelasticity. Most of the evidence for this transition comes from molecular dynamic studies, without viscous drag or hydrodynamic interactions, of around 10^4 particles. Results from such studies share many qualitative features with observations; the finite size of these samples leads to large regimes of supercooling and the absence of realistic hydrodynamics renders them suspect in a number of ways. Moreover, the time scale for simulations corresponds to fractions of a second in real time. Thus, there have been misleading results from early computer simulations that failed to find crystallization in high volume fraction samples. The colloidal system with around 10^{12} particles per cm^3 is truly thermodynamic with well-defined hydrodynamic and potential interactions, and is observed for macroscopic times, thereby avoiding these problems and offering the possibility of defining the equilibrium as well as other kinetic and dynamic processes.

3.6. Limitations of Other Modeling Approaches

Other modeling is rudimentary or non-existent. The experiments proposed here will provide the definitive data that can help guide future modeling efforts.

4. Experimental Details

4.1. Experimental Samples and General Procedure to be Used for BCAT-4

4.1.1. *Colloid-Polymer Mixtures*

The materials and procedures for BCAT-4 are identical to those developed for BCAT-3. We are simply exploring samples in a slightly different position of the phase diagram. From a technical/engineering standpoint, there should be no changes needed to what already has been done and tested extensively with BCAT-3.

The colloidal particles for this experiment will again be poly(methyl methacrylate) (PMMA) particles, stabilized by a thin coating of poly(12-hydroxystearic acid) (PHSA), suspended in a fluid with the same index of refraction composed of *cis*-decahydronaphthalene (decalin) and 1,2,3,4-tetrahydronaphthalene (tetralin), both hydrocarbons. The volume fractions of these samples will range from about 20.92 to 22.37 percent. The polymer will be polystyrene with an average molecular weight of 11.4×10^6 . The colloid-polymer mixtures will be homogenized using a mixing magnet, and then photographed with a digital camera controlled by a laptop running EarthKAM software. We expect their evolution to match the features seen in BCAT-3 phase separation samples: the formation of either a bicontinuous network, or a collection of drops, that ultimately leads to complete phase separation.

4.1.2. *Glass phase vs. crystallization at high volume fractions*

These samples will consist of PMMA particles in decalin/tetralin (the same colloid and solvent materials as the critical-point samples in sec. 4.1.1) at a volume fraction of ~ 0.59 . We expect colloidal crystals to form in these samples, and will use photography to study their evolution, hoping to see white light backlit samples diffract the light so that the color changes with viewing angle. This will help reveal the shape of the nuclei, which provide information about the way the crystals grow in microgravity. The crystallites might grow fast in certain crystallographic directions which could give them a layer like structure. Also their shape will give some hints about the processes that limit the growth. Comparison with analogous ground-based experiments will reveal differences in the growth behavior under microgravity.

4.2. Measurements Required

4.2.1. *Colloid-Polymer Mixtures*

Phase Separation:

- Homogenization by strong shearing
- Time series of 2D color camera images

4.2.2. *Glass phase vs. crystallization at high volume fractions*

Nucleation and growth:

- Homogenization by strong shearing

- Time series of color 2D camera images

4.3. Test Plan including Ground Characterization of Flight Hardware

We emphasize that our experiment has been designed to leverage as much pre-existing technology already resident on ISS as possible. Our only new contribution to ISS cargo will be an exact replica of the sample chamber and mixing magnet used in BCAT-3. All of the other pieces of our experiment, including camera, laptop computer running EarthKAM are already in orbit.

This strategy has resulted in a high level of flexibility and adaptability that has allowed a significant degree of innovation by the astronauts themselves. Even the use of EarthKAM, which increased the quality and quantity of data by more than an order of magnitude, was not suggested and implemented until we had gained several increments worth of experience with manual-only photography. We stress that astronauts Foale, Fincke, Chiao, McArthur and Williams have contributed as much as we have to the procedure currently in use, which has delivered great data to us.

We would therefore greatly benefit by having an exact replica of the entire BCAT-4 apparatus, to facilitate further development of procedures and techniques on the ground, as well as enhance communication with the astronauts actually performing our experiment. Therefore, having a complete set (sample chamber, all holders, camera, and laptop) of apparatus exactly mirroring what is currently onboard ISS would significantly increase the chance of scientific breakthroughs and the success of this experiment.

4.4. Specific Analysis Required

Major parts of the software that will be necessary for data collection and analysis exist already and are being used routinely for the data analysis of ongoing ground based experiments. In particular this includes software for image analysis and particle recognition as well as software for the recognition and structure analysis of colloidal crystals.

4.5. Preflight Experiment Planned

All experiments that are planned for BCAT-4 will also be done before the flight, either with inverted microscopes or on the flight instrument. More details about preflight experiments are given in section 4.3 above.

4.6. Post Flight Data Handling and Analysis

The same form of data analysis will be used after the flight as is used during the flight. Additional software that is required for data analysis will be purchased or written by the principal investigator team.

4.7. Mathematical Models Used

Well-accepted mathematical models representing the physics of fluid mechanics, volume fraction fluctuations, and Brownian motion will be the basis for data analysis of colloid motion in general. For the critical point samples in particular, we take the well-established theory for spinodal decomposition near the critical point as a starting basis for our analysis, recognizing that this does not seem to tell the complete story of what is happening in our colloid-polymer mixtures. We feel strongly that these experiments are meant to provide new ideas and data with which mathematical models can be constructed. Likewise, basic theories and simulations for the nucleation of spherical particles have been developed in recent years, and again we will test the applicability of these models with our experiments in BCAT-4.

4.8. Application of Results

There will be a great increase in our knowledge of the phase behavior of mixtures of colloidal particles of different types, especially for the samples that cannot be density matched. Also, new insight into the crystal structures that are formed by the high volume fraction (high ϕ) colloidal particles as well as the kinetics of their growth; the dynamics and properties of the structures formed will also be gained.

BCAT-4 has a number of applications with a large impact on the everyday life of the general public. Specifically, the colloid-polymer mixtures we study have very close analogs in a number of household products. In particular, fabric softener is composed of vesicles (which behave like colloids) and polymer, added to increase viscosity and improve product performance. The general phase behavior is of great interest to manufacturers (we are collaborating with one very large US company), who want to add more polymer without inducing the phase separation that we are observing in the BCAT samples. They sell around US \$1 billion annually, so a greater understanding of the phase behavior of these colloid-polymer mixtures will have immediate and large impact on an important household product.

Generally, the colloidal nucleation experiment seeks an understanding of the most fundamental liquid/solid transition. Though direct applications of that understanding do not drive the research, growth of ordered colloidal phases has attracted interest in a number of areas, *e.g.* ceramics, composites, optical filters and photonic bandgap materials. Moreover, there is currently great interest in using fields and gradients to control order in self-assembled systems such as diblock copolymers and microemulsions for advanced materials.

5. Experimental Requirements for BCAT-4

The following sections contain specific requirements necessary in order to fulfill the science mission for BCAT-4.

5.1. Sample Description

Colloid-polymer samples and high volume fraction (high ϕ) colloids will be used for these experiments. The PI will provide all these samples for the ground tests and flight experiments. The PI will assure sample quality, cleanliness, and suitability/compatibility for examination over the wavelength range of experimentations.

Flight cell	PI	PI Sample ID	sample class	volume % particles	polymer concentration mg/ml	particle size (diameter)
1	Weitz/Lu	PL101	critical point	22.37	0.797	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
2	Weitz/Lu	PL102	critical point	21.73	0.770	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
3	Weitz/Lu	PL103	critical point	21.51	0.760	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
4	Weitz/Lu	PL104	critical point	21.29	0.749	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
5	Weitz/Lu	PL105	critical point	21.75	0.744	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
6	Weitz/Lu	PL106	critical point	21.06	0.740	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
7	Weitz/Lu	PL107	critical point	20.92	0.733	194 nm \pm 6 nm, 11.4 x 10 ⁶ MW
8	Chaikin/ADH	ADH01	high ϕ PMMA	59	0.00	diameter 0.54 μ m
9	Chaikin/ADH	ADH02	high ϕ PMMA	59	0.00	diameter 0.54 μ m
10	Chaikin/ADH	ADH03	high ϕ PMMA	59	0.00	diameter 0.54 μ m

General notes:

- 1) Maximum volume for all samples is 2.33ml.
- 2) Fluid composition of all samples is 47% decalin and 53% tetralin by volume.
- 3) Composition of all spheres is poly(methyl methacrylate) (PMMA) with a stabilization coating of poly(12-hydroxystearic acid) (PHSA)
- 4) Composition of polymer is polymeric polystyrene (cells 1–7, none in cells 8–10)

5.2. Sample Cell and Instrument Requirements

The sample cell and flight instrument shall have the capability for:

5.2.1. *Sample Homogenization*

For the critical point samples, homogenization should be sufficient to completely mix the sample, so that there is no visible trace of any phase separation. Homogenization shall be sufficient to “melt” the colloidal sample and disperse any existing crystallization. Homogenization must be immediately followed by photography, so that PIs can determine if homogenization is complete, as careful checking requires magnification and processing of the images (clusters of separated phases, whether liquid or crystal, are often not easily visible to the naked eye).

5.2.2. *Optical Imaging*

High magnification, visual imaging of index-matched particles with the digital SLR (Kodak DCS760) is required. For the critical-point samples, the field of view must include the entire sample chamber, and should be illuminated by the camera flash. For the high ϕ colloid samples, field of view should include the entire sample chamber, and additional photos are requested and possibly higher magnification for features (Bragg-scattering crystallites) that form in the sample. To capture these crystallites properly, additional illumination with a mini-MagLite may be required. For both sets of samples, 3 x 12-bit RGB camera-raw images (direct data from the camera at highest resolution and bit-depth) are required, as have been delivered in BCAT-3. An f/stop setting of f/32 is preferred in order to assure the maximum depth of field, which will keep the complete depth of the sample in focus with the minimum amount of effort on the part of the astronaut.

5.3. Sample Cell Requirements

In addition to the sample cell requirements described in section 5.2, the sample cells shall contain the colloidal samples during the length of the experiments, shall provide volumes from approximately 2 mL (*e.g.*, 10 x 20 x 0.1 mm), with rectangular shaped wells to minimize sample volume while maximizing area available for photographing. The sample cells for the critical point samples may have a larger internal dimension because these samples are not as difficult to synthesize. These sample cells shall provide for manipulation and optical viewing of the samples while being contained in a sample holder. It is also essential that each sample cell contain a stirbar, which can be moved by an external magnet to homogenize the sample volume at the beginning of an experimental. Ten sample cells are needed, with more desired.

It is absolutely crucial that the samples be loaded in a clean environment and without any formation of an air bubble in the sample chamber. That is, once the colloid samples are sealed in the glass cuvettes, these must be loaded into the multi-vial sample module in a clean environment, so that no dust enters before the holder is sealed.

5.4. Delivery Requirements

For BCAT-4, it is desired that arrangements be made for late delivery of the samples (2 months or less before launch, preferably less). However, we will take what we can get, while understanding that late stowage requires much less effort for sample homogenization on the part of the astronaut.

5.5. Atmosphere Requirements

Normal pressures and temperatures of the cabin environment should suffice for the samples. For the pure solvents, the temperature should remain above freezing (greater than -40°C preferred, successfully tested to -50°C) and below boiling ($< 190^{\circ}\text{C}$) and such that volume changes do not damage the cells (successfully tested to $+50^{\circ}\text{C}$).

5.6. Vibration Control and Measurement

For the instrument as a whole, the dc component of gravity is most important for this work. An experiment must be long in duration, but needs no better than $10^{-3} g$ averaged over an hour. It is preferable that the critical-point samples not be disturbed when evolving, but this should not be viewed as a constraint that prevents measurements from being performed. In particular, short duration impulses to the ISS environment (*e.g.* from docking operations) are not expected to have any impact on these evolution processes that may take weeks or longer to occur.

If a crystallized sample is disturbed by a significantly strong impulse, its opalescence may disappear; accelerations greater than 10^{-3} could potentially disturb the ordered domains. This experiment is really more sensitive to the lower frequency accelerations. The limit on acceptable average acceleration is given by: $g_{\text{ave}} = 10^{-3} \tau^{-1/2}$, where g_{ave} is the allowable average acceleration, and τ is the time frame of interest, expressed in units of hours. Therefore, over a one hour time frame the allowable average acceleration measured at the sample cell is 1 mg (milli-g). Since the vibration environment cannot be controlled, measurement of the vibrational environment during the mission should provide enough information to determine if samples were disturbed during critical periods.

5.7. Imaging Requirements

Down-linked color images of the samples are needed just before and after homogenization. This will enable the PIs to examine the state of the samples to assess whether full homogenization has occurred before an experiment or equilibration has occurred near the end of a sample run.

In general, the BCAT-3 experiment has benefited greatly from rapid PI access to all of the raw data as very soon after it is collected in-flight. We have had great success with the Digital Imagery Management System (DIMS) Exchange system, allowing the PIs to access and analyze data soon after it is taken on orbit. With rapid communication back to the astronauts, in many cases, we have been able to make significant improvements to our data taking and analysis because of this direct communication. It is therefore crucial to have access to as much data as soon as possible while the experiment is progressing.

5.8. Astronaut Involvement

Astronaut involvement is envisioned for setting up the experiment to be photographed.

On-Orbit Operations and Crew Time Estimate

NOTE: The bold font denotes activities which may or may not occur depending upon when the sessions are scheduled and also whether or not there is crystal formation in Samples 8, 9 and 10. These activity times are pulled out of the total crew times as pending minutes and are expressed separately.

Session 1 (13 Days) Homogenize and Photograph Samples 8, 9, 10, 1, 2, 3; Crystal Check Samples 8, 9, 10

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (if possible here)	10 minutes
Homogenize Samples 8, 9, 10 and 1 (in that order)	
take first photographs manually	120 minutes (for 4 samples)
Photograph Sample 1 automatically for 3 days	--
Perform Crystal Check on Samples 8, 9 and 10	
(any time after the Sample 1 run is complete)	10 minutes
IF crystals are found in 8, 9 and/or 10,	15 minutes
take a few photos of sample(s) then	
submit OCR for more time/photos	
Homogenize Sample 2, take first photographs manually	30 minutes
Photograph Sample 2 automatically for 4 days	--
Homogenize Sample 3, take first photographs manually	30 minutes
Photograph Sample 3 automatically for 6 days	--
Daily Status Check for Samples 1, 2, and 3	
(1 a day for 13 days)	65 minutes
IF no crystals found yet: Perform Crystal Check	10 minutes
on Samples 8, 9 and 10	
IF crystals are found in 8, 9 and/or 10,	15 minutes
take a few photos of sample(s) then	
submit OCR for more time/photos	
Tear down/stow all hardware	30 minutes
TOTAL	6 hours 20 minutes
TOTAL PENDING TIME	40 minutes

Session 2 (16 Days) Homogenize and Photograph Samples 4, 5; Crystal Check Samples 8, 9, 10

Crew FAM	15 minutes
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Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (if possible here)	10 minutes
IF no crystals found yet: If Session 2 began more than one week after end of Session 1, perform Crystal Check on Samples 8, 9, 10 prior to placing Sample Module in clamp	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Homogenize Sample 4, take first photographs manually	30 minutes
Photograph Sample 4 automatically for 8 days	--
IF no crystals found yet: If Session 2 began less than one week after end of Session 1, perform Crystal Check on Samples 8, 9 and 10 after Sample 4 ops	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Homogenize Sample 5, take first photographs manually	30 minutes
Photograph Sample 5 automatically for 8 days	--
Daily Status Check for Samples 4, 5 (1 a day for 16 days)	80 minutes
IF no crystals found yet: Perform Crystal Check on Samples 8, 9 and 10	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Tear down/stow all hardware	30 minutes
TOTAL	4 hours 25 minutes
TOTAL PENDING TIME	1 hour 15 minutes

Session 3 (15 Days) Homogenize and Photograph Sample 6; Crystal Check Samples 8, 9, 10

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (if possible here)	10 minutes
IF no crystals found yet: If Session 3 began more than one week after end of Session 2, perform Crystal Check on Samples 8, 9, 10 prior to placing Sample Module in clamp	10 minutes

IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Homogenize Sample 6, take first photographs manually	30 minutes
Photograph Sample 6 automatically for 15 days	--
IF no crystals found yet: If Session 3 began less than one week after end of Session 2, perform Crystal Check on Samples 8, 9 and 10 after Sample 6 ops	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Daily Status Check for Sample 6 (1 a day for 15 days)	75 minutes
Tear down/stow all hardware	30 minutes
TOTAL	3 hours 50 minutes
TOTAL PENDING TIME	50 minutes

Session 4 (21 Days) Homogenize and Photograph Sample 7; Crystal Check Samples 8, 9, 10

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (if possible here)	10 minutes
IF no crystals found yet: If Session 4 began more than one week after end of Session 3, perform Crystal Check on Samples 8, 9, 10 prior to placing Sample Module in clamp	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Homogenize Sample 7, take first photographs manually	30 minutes
Photograph Sample 7 automatically for 21 days	--
IF no crystals found yet: If Session 4 began less than one week after end of Session 3, perform Crystal Check on Samples 8, 9 and 10 after Sample 6 ops	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Daily Status Check for Sample 7 (1 a day for 21 days)	105 minutes
Tear down/stow all hardware	30 minutes

TOTAL	4 hours 20 minutes
TOTAL PENDING TIME	50 minutes

Session 5 a) If no crystals were found in Samples 8, 9 or 10, homogenize Samples 1 – 10 immediately following Sample 7 Ops, b) Photograph Samples 1 – 10 to ensure they are fully mixed:

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
IF no crystals found yet: Perform Crystal Check on Samples 8, 9 and 10	10 minutes
IF crystals are found in 8, 9 and/or 10, take a few photos of sample(s) then submit OCR for more time/photos	15 minutes
Homogenize all samples	100 minutes
Photograph Samples 1– 10	50 minutes
Tear down/stow all hardware	30 minutes
TOTAL	4 hours 25 minutes
TOTAL PENDING TIME	25 minutes

Session 6 a) Photograph Samples 1 – 10 after they have equilibrated for 6 months:

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
Photograph Samples 1– 10	50 minutes
Tear down/stow all hardware	30 minutes
TOTAL	2 hours 45 minutes

TOTAL CREW TIME for BCAT-4: 26 hours 5 minutes

TOTAL PENDING CREW TIME for BCAT-4: 4 hours

Please note that all the photos are downlinked though EarthKAM, even when the photos are taken manually by the astronauts. Therefore, no astronaut time is required for downlinking photos.

5.9. Data Requirements

On-board data storage requirements:

- All visual images, and other such data should be time-tagged to MET, and GMT.
- Voice annotation of photographs is desired when deemed appropriate by the astronaut.
- Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment.

- All images should be stored with a record of the experimental conditions such as, when the measurement was made, length of measurement, if and how lighting conditions have changed.
- Where possible, temperature should to be recorded whenever photographs are taken. Simply cabin temperature measurements in the area of the experiment will suffice.
- Visual images of samples are desired just before and after homogenization (5.2.1) and periodically (see Science Requirements Summary Table that follows).
- Need capability to periodically downlink any of the above data.

Science Requirements Summary Table

Parameter	Section	Requirement
5.9.1 Samples (compositions)	5.1, 4.1	<ul style="list-style-type: none"> • PHSA-coated monodisperse PMMA particles in an index matching mixture of decalin and tetralin, with and without linear polystyrene particles. • Particle sizes: diameters between 100 and 500 nm. • Index of refraction: 1.511 at the sodium D line at 20 °C • Volume fractions: $0.2 < \phi < 0.74$
5.9.2 Sample mixing	5.2.1	<ul style="list-style-type: none"> • Homogenize samples at beginning of each experiment run (one sample at a time preferred, but not essential).
5.9.3 Optical imaging (visual camera images)	5.2.2 4.2.1, 4.2.2	<ul style="list-style-type: none"> • High magnification, color visual images of colloidal particles; nominally 0.01–5.0µm in size and refractive index matched (to 0.001). • Field of view to include the full length of the sample cells, with additional magnified photographs taken of portions of the sample the astronaut deems interesting (<i>e.g.</i>, dendrites, crystals, droplets). • Images should be taken at maximum camera resolution and bit-depth, and down-linked in the camera-raw (unprocessed) format. • Resolution depth up to 90 µm into a sample of 0.1 optical density; up to 100 µm into the sample is desired. • Record videos at: 30 Hz • Capability for some near real time downlink of video and still images to assist with homogenization (5.2.1) and planning of additional experiment runs. • Note that the capabilities that would be needed for imaging the sample types are: 2K x 3 K resolution, as provided by the Kodak DCS760 camera with a 105 mm focal length lens and the camera set at f/32 (as in BCAT-3).

Parameter	Section	Requirement
Timing of camera images	5.2.2 5.8	<ul style="list-style-type: none"> Photographs are to be taken immediately after mixing, then hourly, or every several hours, controlled by EarthKAM software. Minimum photography requirements: 10 samples x 3 photos per sample = 30 photos per photo session x 4 = 120 photos after 1 day; then 30 x 3 = 90 photos more for a minimum of 210 photos total; plus a repeat (= 420 photos) and hopefully more in between ... say 500 photos.
Wavelength range and respective incident angle range of light source at the sample	5.2.2	<ul style="list-style-type: none"> A flight-qualified mini-MagLite flashlight is sufficient for an illumination source for manually taken photos. And the camera flash with its autoexposure capability is idea when using EarthKAM. The light focus should be adjusted by rotating the lens cap on the flashlight under the light is approximately collimated. This can be verified by moving the flashlight toward and away from a wall and adjusting the lens cap until the spot-size remains approximately constant. The wavelength of the source is fine in the range of 400–700 nm. The angular range should be continuously adjustable to roughly 2.0 degrees resolution in the x-z or y-z planes. There is no coherence length requirement or polarization requirement for the illuminating light source.
Illumination level at the sample	5.2.2	<ul style="list-style-type: none"> Intensity of source light (I_0) will be fixed by the inherent flashlight output. This does not need to be modified unless the batteries are low and need changed. Continuous illumination during photography of Samples 8–10 is desirable. Flash backlighting of Samples 1–7 is desirable.
Angle precision and repeatability	5.2.2	<ul style="list-style-type: none"> The angle at which the most detailed images of any structure (if existent) in a sample cell is visible. This may be in either the forward or backscatter direction.
Camera (or other detector)	5.2.2	<ul style="list-style-type: none"> Kodak 760 camera with a 105-mm focal length lens and the camera set at $f/32$ (as in the later BCAT-3 flight experiments). Images stored on EarthKAM for

		downlinking capability.
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Parameter	Section	Requirement
5.9.4 Sample cell requirements	5.3	<ul style="list-style-type: none"> • Provide adequate containment of the colloidal samples during the length of the experiments. • Sample cell volumes of 2 mL (possibly more for the critical fluids if the plug is removed). • 10 sample cells are needed. • Sample cells must be loaded so that no air bubble is present in the samples • A Teflon coated mixing magnet is inside of each cuvette to allow for homogenization.
5.9.5 Atmospheric requirements	5.5	<ul style="list-style-type: none"> • Normal cabin pressure and temperature environment is sufficient.
5.9.6 Vibration control & measurement	5.6	<ul style="list-style-type: none"> • Averaged over an hour, needs no better than 10^{-3} g of dc g-level; especially after homogenization and prior to measurements, avoid jarring disturbances.
5.9.7 Access to image requirements	5.7	<ul style="list-style-type: none"> • Downlinked color CCD images of the samples are needed just before and after homogenization, and at various stages during crystallization/phase separation.
5.9.8 Astronaut involvement	5.8	<ul style="list-style-type: none"> • Significant during sample homogenization and photography. Approximately 25 incremental hours are required (when available).
5.9.9 Data requirements	5.9	<ul style="list-style-type: none"> • All visual images, and other such data should be time-tagged to MET, and GMT. • Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment if SAMS is running and already available. • All images should be stored with a record of the experimental conditions such as, when the measurement was made, beam and detector positions (forward- or back-illumination measurement, temperature, and any off-nominal conditions (astronaut exercising on bicycle during photography, etc.). • Visual images of samples are desired just before and after homogenization (5.2.1) and periodically. • Need capability to periodically downlink any of the above data.

5.10. Postflight Data Deliverables

- All CCD sample pictures and associated metadata with timestamps and voice annotations of interesting features.
- History of various setting, such as, camera settings (and a note of when and what changes occur in these settings).
- SAMS data if readily available (gravitational acceleration monitoring) in a useful format (*e.g.*, a graphical plot instead of CDs of acceleration data would help us in making use of acceleration information).
- Immediate access to samples: all samples (if available), for further studies at the PI labs, as soon as samples return from orbit, or as soon as possible. It is the glassy volume fraction PMMA samples that are likely to survive the accelerations of a space shuttle reentry. By homogenizing the top or bottom half of the sample and letting it stand, it can be clearly demonstrated that the same sample crystallized in microgravity and not on earth, even with a crystallized surface to initiate crystallization. Not only is such a sample of scientific significance, but the results of this very significant demonstration should be sent to a museum.

5.11. Mission Success Criteria for BCAT-4

Complete success is the achievement of all of the science requirements. This means that there will be sufficient information to provide a crosscheck of all data and calculated factors.

Processing, manipulation and characterization of the samples in microgravity are as important as the measurements during the experiments themselves. For example, sample homogenization is essential to conduct of any of the flight experiments. This allows for the dissolution of the crystallites that have formed in 1-g before launch, and provides a proper starting point in microgravity.

Success Level	Accomplishment
Minimum Success	<ul style="list-style-type: none">• Homogenize and photograph at least <u>six</u> of the ten samples for at least two photo sessions (Req.5.1) – any one from the high ϕ colloidal particle samples, any four phase-separating samples from the colloidal polymer mixtures.
Significant Success	<ul style="list-style-type: none">• Homogenize and photograph all ten samples for at least three photo sessions (Req.5.1) – all the high ϕ colloidal particle samples, all the colloidal polymer samples.
Complete Success	<ul style="list-style-type: none">• Homogenize and photograph all ten samples for at least four photo sessions (Req.5.1) – all the colloidal polymer samples, and all the high ϕ colloidal particle samples.

6. Test Matrix

The current plan for this experiment is to conduct it over five, three-week sessions, which each can be run incrementally and require 4 to 5 hours of crew-time; and a sixth session at six months, which is slotted to take about an hour of crew-time. As such, new information will undoubtedly be learned, and the nature of the experiments conducted will evolve to take advantage of this new information. As a result, it is essential to allow the PIs as much flexibility with the experiment as possible. The test matrices should be viewed as representative of the sort of experiments that will be conducted and can be found in section 5.8, which is titled “Astronaut Involvement”.

7. Principal Investigators' Requests

7.1. Research Equipment

7.1.1. Preflight

We would greatly benefit by having an exact replica of the entire BCAT-4 apparatus, so facilitate further development of procedures and techniques on the ground, as well as enhance communication with the astronauts actually performing our experiment. Therefore, having a complete set (sample chamber, all holders, camera, and laptop) of apparatus for the duration of the experiment exactly mirroring what is currently onboard ISS would significantly increase the chance of scientific breakthroughs and the success of this experiment.

Because the development of our experiment has benefited greatly from the use of tools primarily purposed for other uses onboard the ISS, we would also like to have a list of the available equipment (*i.e.*, not critical components that cannot be moved) that might be potentially used to assist our experiment. For instance, the use of the EarthKAM system has radically improved the quantity and quality of our data. We expect that further improvements could be conceived, and thus would appreciate a list of accessible equipment.

7.1.2. Postflight

Optional access to the flight samples and a functional engineering model of the equipment could allow some of the observations to be tested, and the conditions to be repeated on the ground. This may prove important in interpretation of the data obtained.

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